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A neutron scattering study of the effect of hydrostatic pressure on the incommensurate phase transformation in K_2SeO_4 was performed in order to obtain information concerning the nature of the competing forces that give rise to a structural instability at a general wave vector. It was found that an increase in pressure lowers the transition temperature ($dT_i/dP_i = -6.5$ K/kbar) and results in a smaller value of the initial incommensurate wave vector. The pressure dependence of the incommensurate to ferroelectric phase transition was also investigated ($dT_c/dP_c \simeq -9$ K/kbar). The latter transition displays a distinct pressure hysteresis.

I. INTRODUCTION

It is widely believed that the incomensurate structural transformations that occur in quasi-one- and two-dimensional metals are due to electronic charge-density-wave (CDW) instabilities occurring at the Fermi surfaces.[1,2] It is even clearer that recently studied examples of incommensurate structural transformations in insulators[2] must proceed by other mechanism. A necessary (but not sufficient) condition for a structural instability at a general wave vector is that there exists strong competition between forces of various ranges. This competition is presumably supplied by the oscillation of conduction-electron screening [Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction] in metals. It has been suggested[3–5] that competition between Coulomb dipolar and short-range repulsive interactions is crucial in the case of insulators. The extent to which observations convincingly support the above ideas for either insulators or metals is not overwhelming and additional experimental evidence seems necessary if they are to be tested further. It is in this spirit that the present investigation of the effect of hydrostatic pressure on the phase transformation in K_2SeO_4 was performed.

K_2SeO_4 is perhaps the best studied[6] and best behaved member of a structural class of insulators [including Rb_2ZnBr_4,[7] $(NH_4)_2BeF_4$,[8] and Na_2CO_3 (Ref. 9)] which are susceptible to incommensurate instabilities. (See Ref. 6 for a description of the structure.) The incommensurate transformation is associated with a soft phonon mode with wave vector, $\vec{q}_0 = \frac{1}{3}(1-\delta)a^*$, along the orthorhombic a axis, and $\delta = 0.07$ at the transformation temperature ($T_i = 130$ K at atmospheric pressure) which decreases with decreasing temperature jumping discontinuously to $\delta = 0$ at $T_c = 93$ K. In this low-temperature "locked-in" phase the unit cell triples along a relative to the high-temperature phase and a spontaneous ferroelectric moment appears. Reference 6 presents a Landau theory of these transformations which is reasonably complete and satisfactory on a phenomenological level. According to Ref. 5, the detailed description of the transformation in K_2SeO_4 depends upon a delicate balance of Coulomb and short-ranged repulsive forces.

II. EXPERIMENTAL PROCEDURE

A single crystal of potassium selenate was grown from the saturated aqueous solution by slow evaporation. The crystal was then cut to the shape of a cube with a volume of approximately 0.25 cm^3 and placed in an aluminum hydrostatic pressure cell. The pressure cell was subsequently mounted in a Cryogenics Associates CT-14 flow cryostat. The pressure on the sample could be varied continuously throughout the range from 0.5 to 5.0 kbar with an accuracy of $\pm 2.0 \times 10^{-2}$ kbar. Sample temperature was controlled to within ± 0.05 K.

The neutron scattering measurements were performed on a triple-axis spectrometer in the elastic scattering mode at the Brookhaven High-Flux Beam

Reactor. Pyrolytic graphite monochromator and analyzer crystals were used in conjunction with a pyrolytic graphite filter to suppress the higher-order neutrons. The incident neutron wave vector was 2.549 Å^{-1}.

The scattering measurements were made in the [010] zone. In referring to the incommensurate and ferroelectric phases, it is expedient to introduce the reciprocal-lattice constant $a_L^* \equiv \frac{1}{3}a^*$, so that, e.g., $\vec{q}_\delta = (1-\delta)a_L^*$. We use this new basis in what follows.

III. EFFECTS OF PRESSURE

Figure 1 shows the intensity of the $(4-\delta, 0, 2)$ satellite reflection and the value of δ as a function of temperature at a pressure of 2.1 kbar. Included as the dashed line is the temperature dependence of δ at atmospheric pressure as determind by Iizumi *et al.*[6] The increase in pressure results in a larger value of δ at the onset of incommensurability (and, therefore, a smaller value of the initial incommensurate wave vector $\vec{q}_\delta$) and a lowering of the paraelectric to incommensurate phase-transition temperature from a value of $\simeq 127$ K at atmospheric pressure[6] to $\simeq 116$ K at 2.1 kbar.

In Fig. 2, we summarize the pressure dependence of the lattice constants as well as δ at $T = T_i$. a and c are seen to decrease (almost linearly) with increasing pressure, as would be expected. On the other hand, the value of $\delta(P_i, T_i)$ increases as the pressure becomes greater.

The pressure-temperature phase diagram is represented by Fig. 3. Both the paraelectric to incommensurate and incommensurate to ferroelectric phase-transition temperatures are lowered by an increase in pressure. The latter transition displays a distinct pressure hysteresis and the lower phase line indicated in Fig. 3 is for decreasing pressure. The cross-hatched area is indicative of the extent of the two-phase region at temperatures around 60 K as measured at constant temperature. Presumably the two-phase region extends to both higher and lower temperatures. It is apparent that pressure destabilizes the commensurate phase more than the incommensurate one so that it is unlikely that a direct transformation from the normal to the commensurate phase would occur at even higher pressures. The slope of the phase lines are $dT_i/dP_i = -6.5$ K/kbar and $dT_c/dP_c \simeq -9$ K/kbar for the upper and lower transitions, respectively.

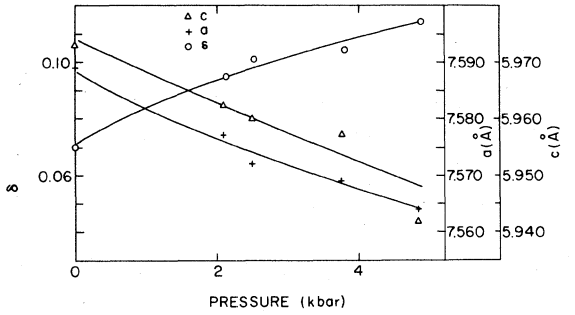

FIG. 2. The values of a, c, and δ at the critical point (P_i, T_i) as a function of pressure.

The paraelectric to incommensurate phase transition is second order[6] and therefore dT_i/dP_i is given by the Ehrenfest relation

$$\frac{dT_i}{dP_i} = \frac{TV\Delta\beta_p}{\Delta C_p} , \tag{1}$$

where $\Delta\beta_p$ is the difference in the coefficient of thermal expansion and ΔC_p the difference in the specific heat at constant pressure just above and below T_i.

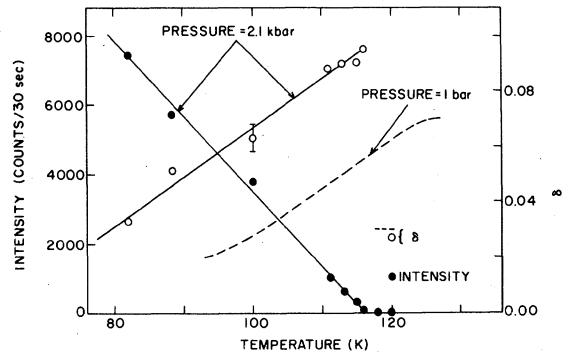

FIG. 1. The intensity of the $(4-\delta, 0, 2)$ satellite reflections and the value of δ as a function of temperature at a pressure of 2.1 kbars. The temperature dependence of δ at atmospheric pressure is after Iizumi *et al.* (Ref. 6).

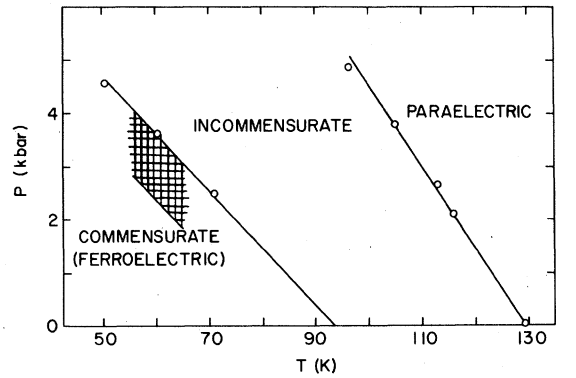

FIG. 3. Pressure-temperature phase diagram for K_2SeO_4. The vertical bar at 60 K is representative of the width of the coexistence region.

Taking values for $\Delta\beta_p$ from the work of Shiozaki *et al.*[10] and ΔC_p from that of Aiki *et al.*,[11] we estimate the value of dT_i/dP_i to be $\simeq -21 \pm 10$ K/kbar using Eq. (1). Because of the large uncertainties involved, more accurate measurements of the thermal expansion and specific heat are required before any quantitative comparison can be made. However, the negative slope is consistent with our findings.

Samara *et al.*[12] have observed a striking regularity in the behavior of dT_c/dP_c for many structural phase transformations. Namely, they found that dT_c/dP_c was negative for soft zone-center phonon instabilities and positive for zone-boundary phonon instabilities, with no known exceptions (at the time of publication). They tentatively interpreted this effect as due to a reversal of roles of short-range and long-range Coulomb forces in the two cases. Of course K_2SeO_4 strictly falls into neither category, but it does seem clear that the critical wave vector involved is far too large to be enhanced by singular $q=0$ Coulomb terms. Thus conceptually, K_2SeO_4 must be considered in the $q \neq 0$ category, and therefore seems to constitute an exception to the relation noted by Samara *et al.* (there appears to be one other known *ferroelectric* exception[13]).

It is hoped that a comparison of the present results with further model calculations of the type discussed in Ref. 5 will lead eventually to an improved microscopic picture. In the meantime, there is one simple manipulation of the results which is possible. It was noted in Ref. 6 that the dispersion of the soft phonon branch as measured by neutron scattering could be Fourier transformed to yield effective "force constants" between entire planes of atoms lying perpendicular to $\vec{a}$. It was found in this way that third-neighbor interlayer forces were dominant over first- and second-neighbor forces whereas fourth- and higher-neighbor forces were weaker still. Figure 4 compares, for example, the measured dispersion of the soft branch at $T=130$ K with that calculated by adjusting the three lowest-order force constants and

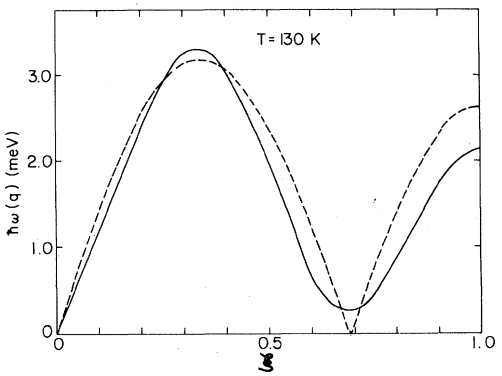

FIG. 4. The measured dispersion of the soft branch at $T=130$ K [after Iizumi *et al.* (Ref. 6)] and that calculated by adjusting the three lowest-order force constants as described in the text. ξ is the magnitude of the wave vector along $\vec{a}^*$ in an extended zone scheme.

neglecting longer-ranged contributions; i.e., we approximate

$$[\hbar\omega(\xi)]^2 = \sum_{n=1}^{3} F_n(1-\cos n\pi\xi) \ , \tag{2}$$

where ξ is the magnitude of the wave vector along $\vec{a}^*$ in an extended zone scheme.[6] Assuming that the transformation remains continuous at higher pressure, the wave vector of the soft mode, $\xi_0(T_i,P_i)$ is then given by Eq. (2) with the additional constraints.

$$\left(\frac{\partial\omega(\xi)^2}{\partial\xi}\right)_{\xi=\xi_0} = \left(\frac{\partial^2\omega(\xi)^2}{\partial\xi^2}\right)_{\xi=\xi_0} = 0 \ . \tag{3}$$

By solving Eqs. (2) and (3) simultaneously using the measured values of $\xi_0(P_i,T_i)$ we can determine the two ratios (F_1/F_3) and (F_2/F_3) at various points along the phase line. The values so obtained are shown in Table I. Notice that the magnitudes of (F_1/F_3) and (F_2/F_3) both increase along the phase line in a way which would be roughly consistent with F_1 and F_2 remaining relatively constant and F_3 de-

TABLE I. Values of the ratios F_1/F_3 and F_2/F_3 of the effective force-constants coupling layers in the crystal separated by a distance $\frac{1}{2}na$ at a number of critical points (T_i,P_i).

T_i (K)	P_i (kbar)	q_δ (units of a_L^*)	ξ	F_1/F_3	F_2/F_3
127.5	0.001	3.930	0.690	−0.233	0.248
116.0	2.10	3.905	0.698	−0.303	0.331
113.0	2.50	3.899	0.700	−0.320	0.351
105.0	3.75	3.896	0.701	−0.329	0.361
96.5	4.85	3.886	0.704	−0.353	0.392

creasing. While the agreement between the measured and calculated curves in Fig. 4 makes it clear that the three-force-constant approximation has limited validity, it does make specific predictions about the pressure dependence of the soft phonon branch. The present sample was too small to investigate the soft-mode dynamics, but we hope to make such measurements in the near future.

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